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Hydrothermal Carbonation of K–Rich Ash, Value Added Energy Engineering and CO_2 Mineral Sequestration

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Abstract

In this paper, hydrothermal carbonation of raw K–rich ash derived from a palm oil plant factory in West Kalimantan, Indonesia had been studied and evaluated at varying temperatures of 50 ºC to 300 ºC, initial CO_2 pressure at between 2 MPa to 2.5 MPa and a maximum final pressure of 8.5 MPa and a residence time of 30 min. The yield of the solid products was about between 47 wt% and 66 wt% and the effective CO_2 content which was captured by hydrothermally solid products was between 0.057 ton · ton^{-1} and 0.115 ton · ton^{-1} following hydrothermal carbonation. In addition, dehydration of solid product occurred at mostly 300 ºC, while oxidation was started at 50 ºC. Obviously, both the sorption–dissociation of CO_2 in the solution and hydrothermal carbonation process produce a global pressure drop in the system resulting in CO_2 mineral sequestration. The carbonation efficiency of solid–fluid interactions at 25 ºC and after 24 h period was 25.36 % and 0.05 954 mol of CO_2 were consumed by the carbonation process. At the condition applied, observed several possibilities were observed such as: the pH (alkalinity), total inorganic carbon, direct precipitation of carbonates minerals as well as crystallization of carbonates in the solution and solid products.

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Keywords: Carbonation; CO_2 captured and storage; CO_2 mineral sequestration; hydrothermal treatment; K-rich ash

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Nomenclature

		L	liter
Al	aluminium	**Mg**	magnesium
Ca	calcium	**min**	minute
CaO	calcium oxide	**MPa**	mega pascal
$Ca(OH)_2$	calcium hydroxide	**wt%**	percent weight
CDM	Clean Development Mechanism, a Kyoto Protocol mechanism to assist developing countries reducing their greenhouse gas emissions	**ton**	10^3 kg
		h	hour
		pH	is a measure of the acidity or basicity of an aqueous solution
		MW	mega watt
CE	carbonation efficiency	**rpm**	revolutions per minute, is a measure of the frequency of a rotation (1/60 Hz).
CO_2	carbon dioxide		
FTIR	fourier transform infrared	**Si**	silicon
g	gram	**SiO_2**	silicon dioxide
GHG	greenhouse gas	**TIC**	total inorganic carbon
Gt	giga ton	**TOC**	total organic carbon
HCO_3^-	bicarbonate/hydrogen carbonate	**UP**	ultra pure
K	kalium/potassium	**XRF**	X–ray fluoresence
K_2O	potassium oxide	**XRD**	X–ray diffraction
Ksp	solubility product constant		

1. Introduction

The consumption of coal for electricity generation is 39.7×10^6 ton of 25 power plants in 2008, with 11 376MW of installed capacity in Indonesia. The use of coal releases proportionately more CO_2 emission than other fossil energy carriers (oil and gas). Indonesian peatland fires are predominantly anthropogenic and source of more CO_2 emission, started by local (indigenous) and immigrant farmers as part of small–scale land clearance activities, and also, on a much larger scale, by private companies and government agencies as the principal method of clearing forest before crops are established. Total CO_2 emissions from Indonesia alone have increased about 38 % from 233.0 in 1998 to 376.3×10^6 ton in 2008 and are projected to increase in the future[1]. This was only one–forth of total CO_2 emission of Japan in 2008 which was 1390.6×10^6 ton. Page et al estimated that between 0.81 and 2.57 Gt of carbon were released into the atmosphere in 1997 from Indonesia as a whole, as the result of burning peat and vegetation[2]. This CO_2 emission will continuously increase with the construction of new coal fired power plant and the increase on the capacity of existing coal fired power plant.

Several evidences of man–made climate change have been accumulating over the past decades. Rising carbon dioxide concentrations due to anthropogenic emissions are scientifically proven to be the main cause for it. One of the alternatives to reduce the CO_2 emission without modifying and/or combined within the energy production system is the retention or sequestration of carbon dioxide in stable geological reservoirs[3–6]. Moreover, the CO_2 dissolution into the pore water and the consequent carbonic acid formation can result in the dissolution of several minerals (mainly carbonate, oxides and hydroxide minerals) affecting the long-term confinement properties of the reservoirs[7]. Although this mechanism favors the permanent CO_2 sequestration, it is expected to be slow in geological formation (hundreds of years) due to the slow kinetics of silicate mineral dissolution and carbonate mineral precipitation.

Various publications[8–13] have proposed the mineral sequestration of CO_2 in controlled reactors as a viable approach to reduce CO_2 emissions into the atmosphere using liquid or solid alkaline residues such as municipal–waste combustion fly–ash, bottom ash, brine alkaline solutions, waste concrete and cements, steel slag, coal combustion fly–ash, alkaline paper mill waste, asbestos, etc. In 1896, a Swedish chemist put forward the idea that

CO_2 emissions from the combustion of coal could enhance the greenhouse effect; leading to adverse catastrophic consequences caused by global warming[14] and has been proved[15]. At present, Indonesia is not subjected to any commitments towards reducing GHG emissions. However, as Parties to Kyoto, Indonesia can voluntarily participate in the CDM and benefit from investments in the GHG emission reduction projects[16].

The objective of the research was to utilize and demonstrate that K–rich ash could be used for the CO_2 sequestered material treated by hydrothermal carbonation. Specific purpose of this research is to estimate the dissolution rate of CO_2 for each experiment as well as to study the kinetic of carbonates precipitation and to understand the carbonation capacity and its mechanism.

2. Material and methods

Raw K–rich ash samples were obtained from a palm oil plant factory in West Kalimantan, Indonesia. The experiments were conducted in a 0.5 L batch–type reactor which has been described elsewhere[17–19]. The amount of the slurry added to the reactor was 300 g, corresponding to 50 g of moisture–free K–rich ash. The reactor was then pressurized with high purity CO_2 to 1.0 MPa, 2.0 Mpa and 2.5 MPa at ambient temperature. Next, the raw peat was heated with agitation at 200 rpm while the reaction temperature was automatically adjusted from 50 °C to 300 °C at an average heating rate of 6.6 °C · min^{-1}. After the desired reaction time of 30 min, the reactor was cooled immediately. After cooling down, the gas products were released through a gasometer and the volume was calculated manually. The solid and liquid phases were then collected from the reactor and separated by filtration using a water aspirator. The liquid product was analyzed for total inorganic carbon (TIC) using a TOC analyzer. The solid products were analyzed by Fourier transform infrared spectroscopy (FTIR), X-ray fluorescence (XRF) and X-ray diffraction (XRD). The photomicrograph and petrography of solid product were analyzed for optical properties and mineral identification by using binocular polarizing microscope.

3. Results and discussion

Table 1 shows the concentration of oxide elements of raw K–rich ash and solid products treated at different CO_2 pressures and temperature as being measured by XRF. Raw K–rich ash contained for about 70 wt% of K_2O followed by Si, Ca, Al and Mg oxides. This ash is rich in alkaline earth elements was possibly contained in palm oil trees and the nutrients from earth or land. Empty fruit bunch has an averagely high ash content for more than 3 wt%, eventhough other wastes generated from palm oil trees such as fiber, shell, trunk and frond has lower K_2O content. As increasing treated temperature and CO_2 treated pressure, CaO and SiO_2 content of solid product increased manifold. While K_2O content in solid products decreased due to the high solubility in water. These indicated that possibly Ca containing carbonates were decomposed and remained in solid products as well as Si.

Development of the carbonation process that affects on oxygen functional explained by using FTIR spectroscopy analysis. Determinations of the peaks in each spectrum of the main functional groups were obtained from several publications[18, 20–21]. Fig. 1 explains about the development of oxygen and other functional group analysis results of raw K—rich ash and solid products. The examination of the (3 500 to 3 100) cm^{-1} zone revealed a progressive lowering in relative intensity of OH stretch content of the solid products produced started at 30 ºC. This peak is somewhat diminished in relative intensity, probably due to the dehydration. The strong bands in the 3 580 cm^{-1} and 3 650 cm^{-1} region are due to the Si–OH stretching modes of silicate clay minerals. Increasing relative intensity of Si–OH stretching with increasing treated temperature is clearly seen in the solid product. Increasing relative intensity of C–O stretching in the form of carbonate (CO_3^{2-}) at 1 420 cm^{-1} and 870 cm^{-1} suggested that carbonation process occurred. In addition, significant changes in the oxygen content of the functional groups can also be observed in the 1 600 cm^{-1} to 1 100 cm^{-1} zone. The distribution of increasing of oxygen content of the functional groups was also observed during the process.

Table 1. Metal oxides concentration in raw K–rich ash and solid products

Metal Oxides	Raw (wt%)	Treated at 2.0 MPa (wt%)				Treated at 2.5 MPa (wt%)			
		50 °C	100 °C	200 °C	300 °C	50 °C	100 °C	200 °C	300 °C
K_2O	68.195	29.589	24.388	21.155	25.555	31.992	20.199	20.255	22.656
SiO_2	8.274	22.961	29.621	33.064	36.928	21.801	34.301	33.301	37.444
CaO	8.178	32.599	28.030	28.828	24.677	34.735	31.609	30.330	25.238
Al_2O_3	5.398	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cl	4.347	1.346	2.334	1.559	1.286	1.656	1.473	1.635	1.018
MgO	2.029	5.912	7.470	8.137	5.676	5.162	4.898	8.044	7.262
SO_3	1.279	0.179	0.000	0.207	0.183	0.000	0.233	0.215	0.196
Fe_2O_3	0.000	1.378	1.314	1.610	1.585	0.000	1.914	0.000	1.583

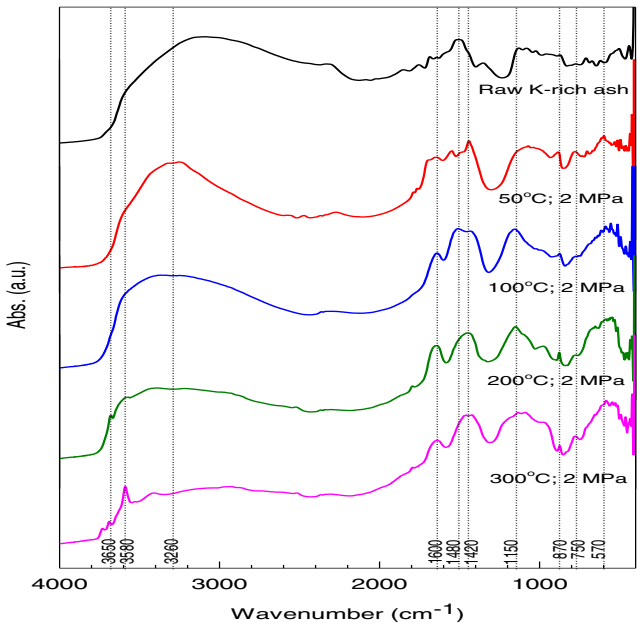

Fig. 1. Typical FTIR spectrum from raw K–rich ash and solid products at selected treated CO_2 pressure (2 MPa)

Decomposition of carbonate and hydration process as a results of hydrothermal carbonation is obviously occured as shown in Fig. 2. Several spectra belonging to a metal halide salt such as KCl are somehow diminished in relative intensity at all treated temperature especially at high angle. These were possibly due to the high solubility of KCl in water at high temperature. Increasing in a relative intensity of carbonate spectra such as $CaCO_3$ including the hydrated forms of carbonate such as $CaCO_3.H_2O$ suggested that carbonation and hydration process are simultaneously occuring when the sample contacted with atmospheric CO_2, dissolved CO_2, water and increasing temperature. Both spectra of $CaCO_3$ and $CaCO_3.H_2O$ increased with increasing CO_2 pressure and temperature. Hydrated forms of $CaCO_3.H_2O$ is diminished in relative intensity at 200 ºC and 300 ºC treated temperature due the dehydration process. Interestingly, that formed of alkaline hydrated magnesium–silicate ($Mg_4Si_6O_{15}(OH)_2.6H_2O$) were only formed at treated temperature of 50 ºC and 100 ºC and at 2 MPa and 2.5 MPa. Other result, related to the formation of SiO_2 which is a major mineralization at high treated temperature and pressure showed to the decomposition of other minerals which are containing K, Mg, Ca partly leached and remained in the solid products.

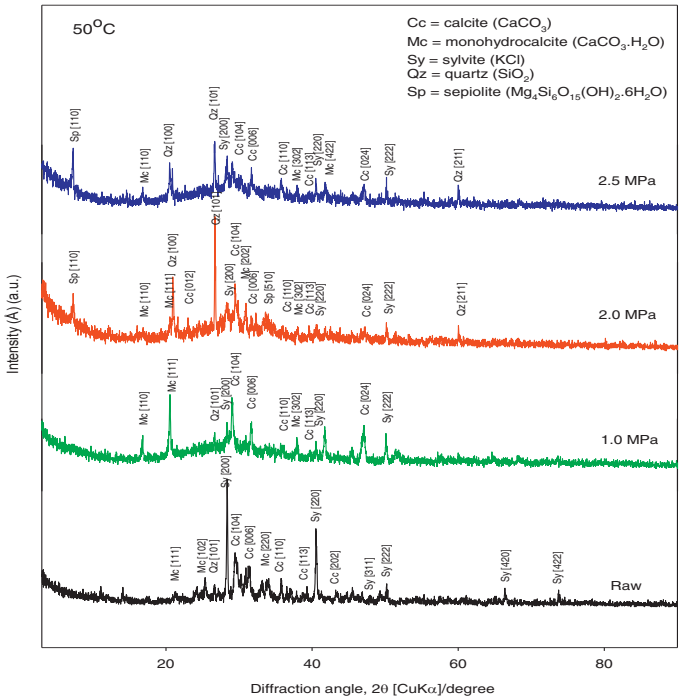

Fig. 2. The XRD patterns derived from raw K–rich ash and solid products at selected 50 ºC and treated CO_2 pressure

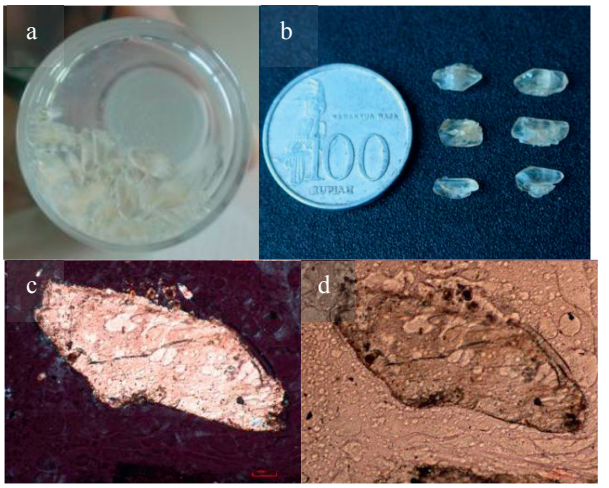

Fig. 3. (a) the photographof precipitated and crystallized products in the liquid products at selected 100 °C and treated 2.5 MPa CO_2 pressure; (b) rhombohedral calcite shape; (c) calcite under cross— polarized light petrography (d) calcite under plane—polarized light petrography

The photograph and petrographical image of solid product identical with calcite crystal. The photograph images of solid product (Fig. 3) commonly showing appearance of transparent–translucent calcite crystal with rombohedral shape which belongs to hexagonal crystal system. The petrographical image under plane–polarized light showing

colorless mineral, with euhedra shape and very high relief. Whereas under cross-polarized light showing high order birefringence colors and simple twinning.

The comparison of XRD spectra of the K–rich ash material and the solid product (Fig. 2), pH, EC and TIC analysis in the solutions and thermodynamic calculations suggest a simple reaction mechanism for CO_2 mineral sequestration by K–rich ash in two successive steps: first, the irreversible hydration of calcium oxide or lime:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (1)$$

second, the spontaneous carbonation of calcium hydroxide suspension:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (2)$$

It was recorded that this global reaction takes place at alkaline pH because the dispersion of the K–rich ash in pure water at atmospheric conditions for solid to liquid ratios for about 20 wt% increases the solution pH up to about 8.7 units (at 100 ºC). The aqueous carbonation of $Ca(OH)_2$ described by the global reaction (3) is an exothermic process[13] that concerns simultaneously the dissolution of $Ca(OH)_2$,

$$Ca(OH)_2(s) \rightarrow Ca^{2+} + 2OH^- \quad (3)$$

and the dissociation of aqueous CO_2,

$$CO_2(aq) + H_2O \rightarrow CO_3^{2-} + 2H^+ \quad (4)$$

these processes produce a fast supersaturation (S_I) of solution with respect to calcite,

$$S_I = (Ca^{2+})(CO_3^{2-}) / Ksp > 1 \quad (5)$$

where (Ca^{2+}) and (CO_3^{2-}) are the activities of calcium and carbonate ions in the solution, respectively, and Ksp is the thermodynamic solubility product of calcite. Then, the nucleation stage (formation of nuclei or critical cluster) takes place in the system,

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \text{ (nuclei)} \quad (6)$$

Finally, the crystal growth occurs spontaneously until the equilibrium calcite and the solution is reached,

$$CaCO_3(nuclei) \rightarrow CaCO_3 \text{ (calcite)} \quad (7)$$

In the present study, the effects of K–rich ash, the CO_2 pressure, the reaction temperature and the reaction time are shown in Fig. 4. Amount of 250 g of ultra and high–purity water with electrical resistivity of 18.2 MΩ·cm at 25 ^oC and 50 g of K–rich ash were placed in a autoclave batch type reactor. The K–rich ash particles were immediately dispersed by mechanical stirring (200 rpm). The experiments were also carried out at room temperature (20 to 25) ^oC. When the dispersion temperature was reached, 1 MPa, 2MPa or 2.5 MPa of CO_2 was purged in the reactor (see Fig. 1). This was the initial pressure of CO_2 which was equal to the total initial pressure in the system. After CO_2 injection, the pressure drop was monitored as a function of time until CO_2 equilibrium pressure in the system (anisobaric system) in order to estimate separately the rate of CO_2 transfer in pure water and during carbonation process from the dispersion as also presented[13].

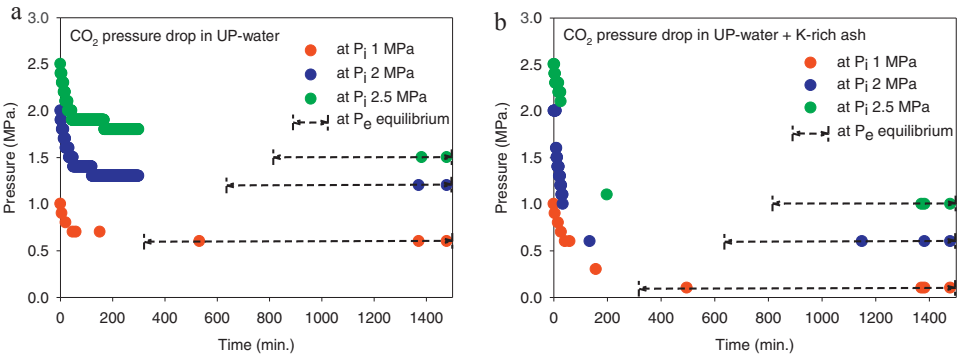

Fig. 4. (a) produced CO_2 pressure drop derived from ultra pure water (UP–water) at room temperature and treated CO_2 pressure; (b) produced CO_2 pressure drop derived from ultra pure water (UP–water) and raw K—rich ash at room temperature and treated CO_2 pressure

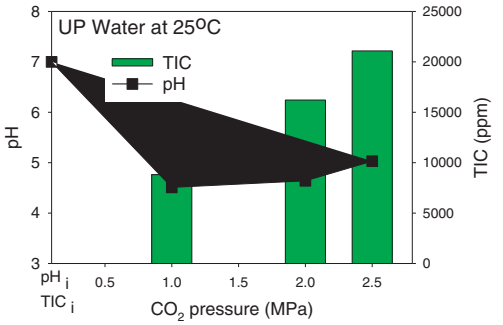

Fig. 5. Recorded pH and TICof the sorption–dissociation of CO_2 in the UP–water at room temperature

Obviously, both the sorption–dissociation of CO_2 in the solution and hydrothermal carbonation process produce a global pressure drop in the system results to CO_2 mineral sequestration. In order to estimate the pressure drop produced by the total process of carbonation, two complementary systems were proposed for each experiment[13]. First, the pressure drop of ultra pure water (UP) related to the sorption–dissociation of CO_2 into pure water only was measured. Secondly, the pressure drop related to the sorption–dissociation of CO_2 in a K–rich ash solution was measured independently. In this second experiment, a concentration of about 20 wt% was chosen, that represented the average concentration after K–rich ash dispersion in water. Recorded pH and TIC of UP–water experiment is representing in Fig. 5 and mostly reaction takes place at acidic pH in a bicarbonate form (HCO_3^-) of its sorption–dissociation of CO_2. These two experiments demonstrated that on the rate of sorption–dissociation of CO_2 of K–rich ash solution was faster than first water system because the monitored pressure drop in pure water was longer to reach the equilibrium pressure as shown in Fig.4.

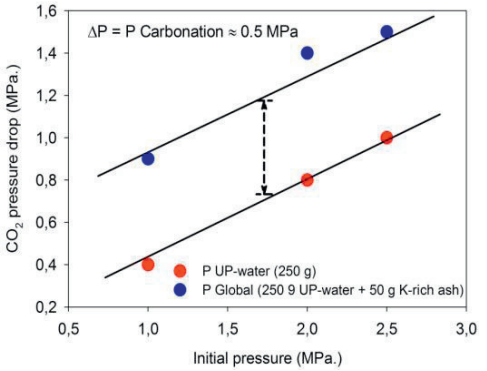

Fig. 6. Linear correlation between the pressure decrease at equilibrium and the initial pressure of CO_2 (from 1 MPa to 2.5 MPa)

A simplified method as describe in reference[13] was developed to estimate the sequestered quantity of CO_2 by carbonate precipitation. Herein, the pressure drop produced by the carbonation process of K–rich ash and ultra pure water in the system was calculated by a simple pressure balance. Consequently, the pressure drop produced by the carbonation process of CaO (8.18 wt%) was calculated by a simple pressure balance:

$$P_{\text{carbonation pressure—drop}} = P_{\text{global pressure-drop}} - P_{\text{water pressure—drop}} \cdot \quad (8)$$

The carbonation pressure drop (P carbonation pressure–drop) was close to 0.5 MPa and it was independent on the initial pressure of CO_2 (1 MPa, 2 MPa and 2.5 MPa) after 24 h of solid–liquid interaction (Fig. 4 and 6). For these experiments, water to fly–ash ratio equal to 10 (w/w) and 30 °C of reaction temperature were used. Systematically, the pressure drop was monitored with the time. These kinetic data showed that the CO_2 equilibrium pressure was reached after about 2 h of K–rich ash–fluid interaction. In contrast, the CO_2 equilibrium pressure in pure water was reached after about 3 h. This means that the carbonation process enhances the rate of CO_2 transfer in the system. Considering that CO_2 is an ideal gas, the quantity of CO_2 consumed by the carbonation process can be calculated as follows:

$$n\text{CO}_2 = P_{\text{carbonation pressure—drop}} V / \text{RT} \quad (9)$$

where, the V is the reactor volume occupied with gas (0.5 L), T is the temperature of reaction (≈303 ◦K) and R is the gas constant (0.08314472 L bar/°K mol). Using the calculated value $P_{\text{carbonation pressure—drop}}$ = 0.5 MPa, as calculated that 0.0925 mol of CO_2 were consumed by the carbonation process. Taking into account reactions (2) and (3) and the fact that the K–rich ash contains 8.178 wt% of lime (CaO), the carbonation efficiency CE can be calculated by the following expression:

$$\text{CE} = n\text{CO}_2 M\text{CO}_2 / (w\text{CaO}/M\text{CaO})\, M\text{CO}_2 \times 100 \quad (10)$$

where, $n\text{CO}_2$ is the mol number of consumed CO_2, calculated by Eq. (9) (0.0925 mol), $M\text{CO}_2$ is the molar mass of CO_2 (44.01 g/mol), wCaO is the starting mass of CaO in the reactor (4.1 g) and MCaO is the molar mass of CaO (56.077 g/mol). The carbonation efficiency was then calculated to 25.36 % after 24 h of solid–fluid interactions at 25 °C.

The monitoring of the pressure drop for any controlled system under ideal gas conditions allows the kinetic modelling of CO_2 transfer after gas injection in an aqueous solution or in a solid–liquid system (K–rich ash–water dispersion for this study) as described in reference[13]. This can be done using a simple correlation function, $n_{\text{total}}\ \text{CO}_2 = \text{f}(t)$, where $n_{\text{total}}\ \text{CO}_2$ is the total mol quantity of CO_2 to be sequestered in UP–water or in the K–rich ash–water dispersion and t is the time after gas injection. For this case, the best fit (attested by a correlation factor close to 1) of the experimental–calculated data was achieved when using a pseudo–second–order kinetic model according to the following expression:

$$\text{d}\, n_{\text{total}}\ \text{CO}_2,\text{t} / \text{dt} = k_s\, (n_{\text{total}}\ \text{CO}_2,\text{max} - n_{\text{total}}\ \text{CO}_2,\text{t})^2 \quad (11)$$

where ks is the rate constant of sequestered CO2 (1/mol s) for a given initial pressure of CO_2 in the system, $n_{\text{total}}\ \text{CO}_2$,max is the maximum sequestered quantity of carbon dioxide at equilibrium [mol], $n_{\text{total}}\ \text{CO}_2$,t is the sequestered quantity of carbon dioxide at any time, t (mol).

The integrated form of Eq. (11) for the boundary conditions t=0 to $t = t$ and $n_{\text{total}}\ \text{CO}_2$,t = 0 to $n_{\text{total}}\ \text{CO}_2$,t = $n_{\text{total}}\ \text{CO}_2$,t is represented by a hyperbolic equation:

$$n_{\text{total}}\ \text{CO}_2,\text{t} = n_{\text{total}}\ \text{CO}_2,\text{max}\ \text{t} / (1/\text{ks}\ n_{\text{total}}\ \text{CO}_2,\text{max}) + \text{t} \quad (12)$$

In order to simplify the fitting of experimental–calculated data[13], have defined the constant $t_{1/2}$= ks$n_{\text{total}}\ \text{CO}_2$,max has been defined. Physically, $t_{1/2}$ represents the time after which half of the maximum sequestered quantity of carbon

dioxide was reached and is called "half–sequestered CO_2 time". It can be used to calculate the initial rate of CO_2transfer, $v_{0,s}$ (mol/s).

$$v_{0,s} = n_{total}\ CO_2,max\ /\ t_{1/2} = ks(n_{total}\ CO_2,max)^2 \quad (13)$$

The parameters $t_{1/2}$ and n_{total} CO_2,max were estimated by applying a non—linear regression using the least—squares method. The initial rates of CO_2 transfer in UP–water and in water–K–rich ash suspension were calculated using Eq. (13). These results demonstrated that the initial rate of CO_2 transfer was enhanced by carbonation process for our experiments. In addition, it's well known that the CO_2 solubility in UP–water increase with an increase of pressure. The present study showed that initial rate of CO_2 transfer in pure water also increases with pressure (from 1 MPa to 3 MPa) (Fig. 7).

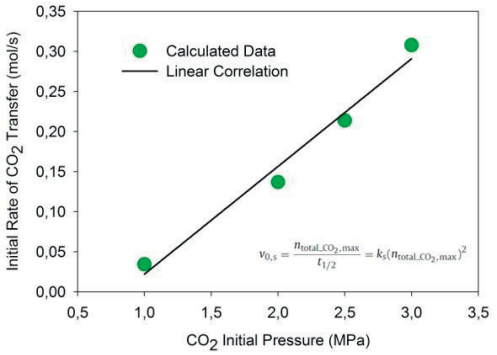

Fig. 7. linear increase of initial rate of CO_2 transfer with CO_2 initial pressure (from 1 MPa, 2 MPa, 2.5 MPa and 3 MPa)

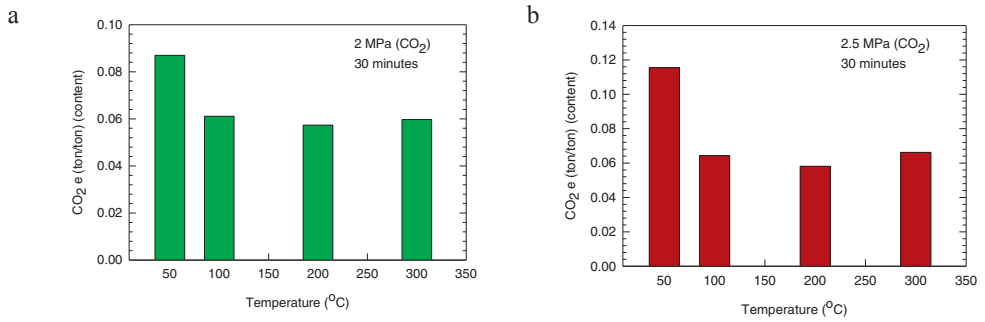

Fig.8. (a) the amount of CO_2 content in hydrothermally treated solid product of K–rich ash at 2 MPa CO_2 pressure; (b) the amount of CO_2 content in hydrothermally treated solid product of K–rich ash at 2.5 MPa CO_2 pressure

Fig. 8. explained the amount of CO_2 content in hydrothermally treated solid product of K–rich ash. These indicated that as increasing treated temperature results in decreasing of CO_2 content in hydrothermally treated solid product. As increasing of treated pressurized CO_2 gas results in increasing of CO_2 content in hydrothermally treated solid product. At 50 °C, both treatment at 2.0 MPa and 2.5 Mpa of pressurized CO_2 gas has the maximum CO_2 content of solid products at 0.087 ton · ton^{-1} and 0.115 ton · ton^{-1} following the hydrothermal carbonation respectively.

4. Conclusion

In this research and study, hydrothermal carbonation of raw K–rich ash was evaluated at temperatures ranging from 50 °C to 300 °C at purged CO_2 gas of 2.0 Mpa and 2.5 MPa, a maximum final pressure of 8.5 MPa and a residence time of 30 min. Raw K–rich ash has potentially for the CO_2 sequestered and captured material. The

sequestered capacity of the K–rich ash depends on the treated temperature and purged CO_2 gas. Also, it was to demonstrate the feasibility to use K–rich ash to sequester CO_2 under mineral form via CaO carbonation. The results revealed a significant significant CaO—$CaCO_3$ chemical transformation by using a simplified pressure–mass balance method. In addition, the kinetic data demonstrated that the initial rate of CO_2 transfer was enhanced by carbonation process in our experiments.

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